

DEVELOPMENT OF REPLICATED  
OPTICS FOR  
AXAF-I XDA TESTING

Final Report  
May 1995

Contract No. NAS8-38609, D.O. 111  
UAH Account No. 5-33510

Submitted to:

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Title: **Development of Replicated Optics for AXAF-I XDA Testing**

**Objectives in SOW:**

- (1) Prepare replication samples of electroless nickel coated aluminum. Determine process requirements for plating XDA test optic.
- (2) Prepare and assemble plating equipment required to process a demonstration optic.
- (3) Characterize mandrels, replicas and test samples for residual stress, surface contamination and surface roughness and figure using equipment at MSFC.
- (4) Provide technical expertise in establishing the processes, procedures, supplies and equipment needed to process the XDA test optic.
- 5) Reports - Three Quarterly and Final.

**1.0 SCOPE AND PURPOSE**

Advanced optical systems for applications such as grazing incidence Wolter I x-ray mirror assemblies require extraordinary mirror surfaces in terms of fine finish and surface figure. The impeccable mirror surface is on the inside of the rotational mirror form. One practical method of producing devices with these requirements is to first fabricate an exterior surface for the optical device then replicate that surface to have the inverse component with lightweight characteristics. The replicate optic is not better than the master or mandrel from which it is made. This task identifies methods and materials for forming these extremely low roughness optical components.

## 2.0 MANDREL IMPROVEMENT STUDIES

### (a) Electroless Nickel Coated Aluminum Samples

The actual requirements for the x-ray mirror components are surfaces after replication to be achieved with sub-nanometer surface finish. Ideally the surface should be as smooth as physically possible. To date the smoothest surfaces known over any appreciable span are flat circular coupons of crystalline silicon carbide formed by chemical vapor deposition (CVD) at MORTON International. These surfaces reportedly were prepared on the CVD pieces by Dr. Jean Bennett of US Navy Weapons Center in China Lake, California. Some samples are reportedly measuring less than one angstrom Rms by WYKO interferrometry using measurement methods also reported by Dr. Bennett. UTOS of Florida also has polished the silicon carbide samples to achieve similar surfaces. One of these samples available to UAH for study indeed measures between one and three angstroms Rms by the described method.

The available SiC sample has been used as a guideline to produce samples with low surface roughness using machinable materials such that actual x-ray mirror mandrels can be produced. The piece actually conducts sufficiently well that by vacuum coating a thin gold film it was possible to pass current directly through the SiC and electroplate a nickel piece. The replicated piece with a gold layer then separated easily and the inverse replication was indeed about 3 angstroms Rms with some values about 5 angstroms Rms due to some deformation in the electroformed nickel. This demonstrated that given a surface sufficiently smooth, a replicate surface could be returned which is well under the 10 angstrom (1 nanometer) goal.

Approximately 60 aluminum samples total have been single point diamond machined and are being used for this study. Forty of the samples have been plated with electroless nickel ranging from 8% to 13% phosphorous by weight. The electroless nickel coating applied can be either directly polished or returned with the single point diamond turning process and then polished. Electroless nickel plated aluminum samples plated with nominally 11 Wt% phosphorous for surface finish and passivation studies have been completed. The aluminum alloy used is 6061-T6 hardness which is easily machined by single point diamond turning. A major drawback has been the electroless nickel plating process instability.

The analysis and maintenance of the electroless plating solution and overall process is very critical if quality such as required for x-ray mirror applications is to be achieved. Additional support has been recently provided for the plating, polishing, surface finish measurements and data recording efforts to establish procedures for producing the best possible surfaces.

The electroless nickel high quality plating process from Stapleton Inc. has produced very fine nickel alloy surfaces but at the expense of instability and very slow deposition rate.

This required considerable additional support from the materials group. The substitution of a smaller plating tank and support equipment has been completed. The solution has also been replaced with Enthone Corporation ADP-300 (QA) process which to date appears to be more stable and consistently produces a given alloy at somewhat higher plating rates. This process has been studied in detail to determine the optimum conditions to achieve phosphorous concentration from about 9% P to about 13% P maximum. See Appendix I.

Lapping results to date demonstrate that this Enthone process will produce lapped parts which meet or exceed the required 10 angstrom Rms level when either diamond turned a second time or when directly lapped after plating using either diamond paste or aluminum oxide compounds. The objectives have now been moved upward to seek a continuous surface of  $\leq 5$  angstroms Rms. Unfortunately on two occasions the second diamond turning step, which was on the plated nickel, encountered programming problems which permitted the nickel phosphorous coating to be removed or damaged to the depth of the aluminum. This resulted in the destruction of twenty of the nickel phosphorous plated samples. An additional contract has been defined to continue the study.

The polished mandrel surface of electroless nickel which produces the best polished surfaces appears to consistently be the  $\text{Ni}_3\text{P}$  ratio of 11% phosphorous by weight which has been plated on aluminum (6061 - T6). The average polished surface finish of one mandrel from the Enthone process is consistently less than ten angstroms Rms. Others to date measure above ten angstroms.

Due to schedule loading for other contracts at MSFC, it was not possible to complete the polishing tests within the time frame for this contract. Therefore samples of plated nickel were sent to outside vendors for polishing evaluations. OCA has plated an additional 10 parts. Seven of these have been polished also by OCA. The process was not completely revealed but essentially consisted of polishing with successively smaller diamond and finishing with colloidal silica.

The surfaces achieved measure consistently less than ten angstroms Rms by WYKO at 20X with many values in the range of three to six angstroms. The primary uncertainty in the surface quality includes the possibility of residual colloidal silica in low valleys which may improve the observed quality of the polished metal surface but depending on subsequent processing steps to form the x-ray replicate optic, may be released to leave a film of silica within the optical shell.

Any foreign material is very difficult to remove from an optical surface and particularly difficult from the gold layer within the replicate. This difficulty is pre-eminent whether the gold is vacuum evaporated or electroplated onto the mandrel. In the case of the silicon carbide it is not possible to determine if silica was used in the polishing since chemically it would be detected as silicon since the presence of oxygen is nearly always detected on a surface exposed to air. However for other materials such as the electroless nickel the use of ESCA will hopefully help determine the level of contaminants such as residual silica by the detection of silicon.

(b) Vacuum Deposited Gold for First Optical Surface

Two methods of depositing the first surface for the mirror using gold are under investigation. The first is to deposit gold using an evaporation process in a vacuum system. The second is to passivate the nickel surface and deposit gold by electrodeposition from an aqueous electrolyte. This requires that the lapped surface be subjected to an electrolytic process to form an oxide containing nickel, phosphorous and oxygen. The details of this process were reported in the final report for NAS8-38609 D.O. 63.

The second process has since been automated to provide a controlled ramp-up rate for the oxidizing current and an automatic cut-off for the current when a specific surface potential is reached. This work was performed by Paul Wilkins of The George Washington Univ./NASA Langley Research Center in conjunction with UAH/NASA MSFC. See Appendix II.

Two electroless nickel coated parts have been passivated using the computer controlled process to control the rate and thickness of the oxide film formation. WYKO measurements before and after this treatment on two occasions returned no discernible difference in the mandrel surface finish before and after passivation and the average surface finish appeared to be slightly better after the first passivation test and with no change discernible after the second test.

To compare the effects of replication from the nickel phosphorous directly or from the electrochemically oxidized nickel phosphorous, evaporative deposited gold is to be evaluated against electrodeposited gold replicated on polished electroless nickel substrates and backed with at least 0.5 millimeters of low stress nickel. A fixture has been built to hold the parts during the electroplating to achieve a uniform deposit uniformly low stress. Parts available will be evaluated with electroplated and evaporated gold coatings as the replicate surface. This effort will be extended since the electron beam evaporation vacuum coating system used for this task is presently under repair.

Therefore the present resolution has been to coat three of the nickel plated aluminum coupons in building 4711 (Robert DeHaye). The samples were cleaned with acetone and then gold coated to a thickness of about 1000 angstroms with no further preparation. After electroforming nickel about 0.5 millimeters thick, and separating the form, the replicate returned only about 10 - 12 angstroms rms although the original surface of the mandrel had been measured at 6 - 10 angstroms rms. There appeared to be contamination embedded in the gold starting surface. A second sample was prepared from a stainless steel (410) substrate using the electrolytic gold. This piece measured about 10 - 12 angstroms at the start. The gold did not adhere at all well to the stainless steel and plating solution leaked in under the edges. However the center portion of the replicate was still about 10 - 12 angstroms rms.

Additional tests were conducted on the 410 stainless steel piece polished to about 10-12 angstroms rms. The replication was performed without the gold. The first replicate form was almost perfectly matched to the substrate with the surface finish at 10-12 angstroms and the curvature minimally detectable compared to the curvature of the mandrel. A second replicated nickel piece has been made from the same mandrel and is again a very close match with an rms value returned at about 11 angstroms and a curvature of virtually zero. Tests are ongoing and the replicate comparison of the electrolytic gold with the passivation process will be continue to be compared to the vacuum system deposited gold.

(c) Conductive Oxides, Carbides and Refractory Metals for Improved Mandrel Surfaces

A mandrel coated with a very hard amorphous or microcrystalline ceramic material which conducts electrically in an electrolyte, provides a more desirable substrate for the fabrication of x-ray quality mirrors than electroless nickel if it can be polished to the same quality as has been seen with silicon carbide.

If such a substrate were non-conductive the first surface which replicates the mandrel could still be applied by vacuum coating procedures so long as separation were possible.

Also if the entire mandrel were made of a material which was lower thermal expansion than the electroformed nickel shell then the release could be achieved by heating rather than cooling the system thus eliminating the condensation issues.

Indium tin oxide, chromium carbide, silicon carbide and tungsten carbide are candidate conductive hard ceramic coatings which should be possible to achieve at lower temperature using RF sputtering or electron beam melting procedures for vacuum deposition.

All four coatings should survive the chemical environment for plating electrolytic gold and should be possible to apply to the polished electroless nickel. Selected deposits have been coated over polished electroless nickel/aluminum and glass slide substrates and polished to the best achievable finish then measured. An attempt to plate a high molybdenum alloy containing trace titanium and zirconium (TZM) was made using E-beam heating of the target but the process used produced a very poor coating. Samples of pure molybdenum on glass have been coated by Dr. M. Wilson of UAH and were very smooth and coherent with surfaces of float glass at a few angstroms rms being essentially preserved on the back surface of the Molybdenum. These samples were not available to this project however for the replication study. It is felt that a much better molybdenum coating is achievable.

Samples of indium tin oxide coated glass were obtained from Dr. Palmer Peters and measured by WYKO interferometry. The coatings were also measured for conductivity and ranged from a high of 370 to 400 ohms/square to a low of 60 to 70 ohms/square and the roughness increased accordingly with the lower resistance a function of the thicker deposit. The smoother coatings were about 8 - 15 angstroms on the average. The electroplated nickel was directly applied to the ITO and separated with surfaces very nearly matching the starting values. Attempts to polish the ITO with 0.1 micron alumina resulted in rapid removal of the coating. It was not possible to electroplate gold directly on the ITO samples due to the high cathodic overpotential of the ITO compared to the gold process used.

Samples of vacuum deposited silicon carbide on glass were also obtained from Dr. Peters. These samples measured about 7 - 10 angstroms rms by WYKO and did not conduct sufficiently well to be electroplated with nickel or gold. The use of a vacuum deposited gold will be required if this type coating is used.

A sample of polished silicon carbide furnished by Morton International on a separate contract to Chrysler Corp. Pentastar division, was used as a measurement standard for the UAH and MSFC WYKO instruments and also the MSFC AFM. This sample appears to consistently return between 0.9 and 3.2 angstroms rms depending on the measurement method and location on the sample.

A plating replicate sample was made from this piece and it was found to be sufficiently conductive to support the nickel plating direct but again not the gold. The sample was coated by evaporation with gold and electroplated with nickel. The deposit was readily separated by using increased temperature differential but without any prior passivation process. The replicated gold/nickel surface was about 5 angstroms rms with some of the disturbance apparently distortion as described earlier. Measurements of the silicon carbide surface after the replication revealed no change.

Additional very desirable coatings may follow from the tool coating industry established by Balzers Inc. The capability to coat tools with titanium and chromium nitrides and carbides is well established and a very large commercial business. These coatings are very hard and inert chemically. The major drawback is that the coatings must be deposited at about 950 degrees fahrenheit using the present Balzers physical vapor deposition (PVD) process. Preliminary tests on electroless nickel plated aluminum coupons were not successful due to the larger expansion of the aluminum which was encapsulated by the nickel. When the samples were heated to the required temperature the nickel cracked and flaked off.

The Balzers engineer provided samples of four coatings on steel for evaluation. The samples are TiN (titanium nitride), TiCN (titanium carbon {or carbo} nitride),  $\text{Cr}_3\text{C}_2$  (chromium carbide) and CrN (chromium nitride). The substrates were not prepared optically and as such the coatings were accordingly very rough as optics. The deposits are very thick at about 3 - 5 micrometers, and indeed are extremely durable. A sample of the Balzers titanium nitride coating on steel was selected for polishing. After about one hour of polishing with 3 micrometer alumina it was apparent that the sample was too rough to achieve a respectable surface by hand polishing in that fashion. Subsequent tests showed that silicon carbide sandpaper up to 400 grit would eventually move the surface towards an improved quality. Diamond or alumina in excess of 9 microns, used as loose abrasive, caused chipping and brittle failure of the titanium nitride coatings. However after about two to three hours of hand polishing with successively finer grit SiC paper down to 2000 mesh, the sample was hand polished with 3 micron alumina followed by 1, 0.3 and 0.1 micron alumina for about 30 minutes each. The surface still was not penetrated to the steel which is considered phenomenal.

WYKO measurements showed this crude polishing process on a very rough starting sample had produced between 5 and 12 angstroms rms surface finish. There was evidence of shallow pitting in the sample surface which is believed to be due to the substrate. This sample has also been used for a replication test and the material was found to be sufficiently conductive to support both nickel and gold deposition directly.

The sample was electroplated with gold about one micron thick followed by about 50 microns of nickel which was then readily removable. No special activation processes were applied other than to clean the sample prior to plating.

Additional work in this area will proceed with Dr. M. Wilson as PI under D.O. 139. The replicate plating will be performed from the prepared samples by D. Engelhaupt.



Samples of 410 stainless steel have been prepared by conventional machining followed by heat treating to 1850 degrees fahrenheit and quenched with nitrogen gas. These parts were then lapped on an automated polisher using successively smaller diamond abrasives to rapidly produce surfaces in the regime of ten angstroms Rms with many readings achieved near seven or eight angstroms Rms. Subsequently 15 samples have been coated (three each) with titanium nitride and carbo-nitride and chromium nitride and carbide. The TiN was coated onto the 410 stainless pieces with two processes. These samples were coated by Balzers in Tonawanda, NY and returned. The TiN samples coated by the Balzers designation "mirror block" process are very reflective and smooth. Data on the polishing and measurements will commence on the UAH D.O. 139 and will be monitored by Dr. Michele Wilson of UAH/CAO. These samples will then be used to produce replicates of gold/nickel surfaces similar to the electroless nickel.

The objective of D. O. 139 will then be to determine if the same materials which perform best can be produced at MSFC by lower temperature processes such as ionization enhanced deposition of electron beam melted titanium with codeposition of nitrogen from the ionized plasma. This would permit the refractory conductive coatings to be applied to lower temperature sensitivity substrates such as the diamond turned aluminum and electroless nickel coated aluminum pieces which could much more readily be fabricated in the shapes and accuracy required for the x-ray mirror mandrels. This task is also the responsibility of Dr. Michele Wilson.

(d) Develop Alternate Electrodeposit for Mandrels -

A deposit is desired which can be electrodeposited over aluminum or other materials and single point diamond machined and polished. The electrolytic processes are typically far less troublesome than the highly volatile, hot electroless solutions which spontaneously decomposes with use. Note that this is an addition to the original task and is not in the SOW so the effort was non interfering in scope.

Electroless nickel phosphorous alloy is presently used to coat aluminum for the purpose of producing mirror surfaces. The electroless nickel plating processes are not as easily applied as an electrolytic coating. This is due to a number of reasons but particularly true due to the need to replace the nickel and phosphorous chemically rather than from a soluble anode system. Also the deposit is attained at a very high temperature near boiling which requires special equipment and handling. The solution constantly decomposes such that after a fixed amount of deposit is acquired per unit volume of solution then the solution must be salvaged for nickel or sent to a chemical waste treatment facility. The electrolytic pure nickel plating processes do not produce a deposit which is readily diamond turned and polished.

Normally the crystalline deposits of nickel form carbides with the diamond tool cutting edge and very rapidly degrade the edge surface of the tool.

If a nearly amorphous electrolytic nickel deposit can be attained with the use of appropriate additives it should be possible to diamond machine the material without significant damage to the tools in a normal tool life span. Previous attempts by several researchers to electrodeposit nickel phosphorous have not been successful in producing high quality deposits. It has been possible to achieve a very fine grain structure nickel through the use of additives other than phosphorous. This type deposit was explored briefly for compatibility with optical fabrication processes.

A solution of nickel sulfamate containing two organic additives, 1,3,6 naphthalene trisulfonic acid and coumarin was used to plate a small cylinder. This deposit was then turned by UAH using a conventional zero rake diamond tool. The surface was not as good as turned nickel phosphorous and returned only about 300 angstroms surface finish. Polishing of this surface did improve the surface rapidly with about 20 - 30 angstroms achieved. No further effort was put into this piece pending turning with a diamond tool of -5 degrees rake angle.

#### (e) Hybrid Composite / Plating Combinations

Recent efforts involving replicated x-ray optics have shown that a filament wound composite over a mandrel which had a thin reflective coating would show serious distortion of the surface due to the residual stresses in the winding upon curing. By application of a layer of electroformed nickel and by adding the epoxy composite as a cured shape with similar thermal expansion such as E-glass filled material rather than winding, it should be possible to eliminate or at least minimize this effect.

Since winding is not a requirement for this approach the sample preparation without induced mechanical stress should minimize the amount of surface distortion. Circular disks or conical pieces will be coated with gold and then a substantial layer of nickel will be electroformed (0.2 millimeter). The cured epoxy composite shape will be applied next with a thin layer of epoxy and allowed to cure. After curing, the composite and the metallization will be separated from the mandrel and the replicate surface measured.

Tests can be performed using the plating stress monitor to observe the stress during composite curing. This will require some form of temperature feedback to the instrument for stability. This process will be tested under the renewed contract in 1995.

(f) Non-magnetic Optical Electroforms

This activity is suggested to replace nickel as a mirror shell material in those applications where magnetic materials could affect other instrumentation such as inertial guidance devices.

Copper is the most commonly used material for electroforming non-magnetic shapes. Pure copper has very poor mechanical properties compared to nickel and as such the deformation will be difficult to control unless the weight is substantially increased. Nickel phosphorous such as plated with electroless nickel process is strong and non-magnetic but historically would be very difficult to plate into free standing shapes with electroless (catalytic) or electrolytic procedures. Copper alloys are viable candidates with bronze or brass possessing adequate mechanical properties to compete with nickel. Also the yield properties of copper electrodeposits can be substantially improved through the use of additives which act as grain refiners to increase the number of blocking sites in the material.

This activity will be limited in scope to a demonstration of a non-magnetic test piece of high surface quality replication and low residual deformation from intrinsic stress. This activity will also occur during the 1995 contract effort.

(g) XRCF Mandrel Fabrication

The first mandrel for a prototype XRCF mirror electroformed shell has been completed by MSFC. The shielding and end pieces were designed by UAH and have been fabricated by MSFC.

The electroless nickel was plated to a thickness of 0.008 inches instead of the previous 0.004 - 0.005 inches used in order to cover a defect in the mandrel caused by machining. The defect was not completely removed after diamond machining.

This piece was used to study the electroforming process without preparing an x-ray qualified surface by extensive lapping efforts. The plating involved testing of the automated passivation setup although the decision was made to coat the mandrel with gold from the electron beam Balzers vacuum coating system. Nickel plating thickness uniformity and zero stress conditions were studied using a part which was only rough machined. This required measurements of the current density with the eddy current probe used on AXAF-S and fixture or anode adjustments to assure the uniformity of the current density. A plating fixture was purchased designed to plate the part horizontally in the electrolytic plating process. This is to insure that the edge effects are minimized to eliminate the need to trim the ends of the mirror by machining or grinding as before. The plating proceeded with very good uniformity but the part had a very sharp razor blade type growth up the sides of the RTV seals between the

sections. The RTV had previously been soaked in dilute sulfuric acid to assure that no ionic materials were present. However the RTV appeared to absorb enough of the nickel and acid from the plating bath to conduct and plate. The RTV also may have contained a small amount of carbon although this was not verified. Tests on the rough machined part have subsequently been performed using Teflon seals with no detectable growth on the seals.

A second electroless nickel plated mandrel has been diamond turned using the new Pressotech turning center and achieved 25 angstroms rms directly off the machine. This piece has been polished to a surface of 3 - 6 angstroms rms using only alumina and to date is the best x-ray mirror mandrel produced.

The above information will be used to establish improved processes for replicated optics in general. Also the actual fabrication of AXAF-I XDA and XRCF test optics will follow from the preferred processing methods determined by the test pieces.

### **3.0 SUMMARY OF RESULTS TO DATE**

#### **(a) Electroless Nickel Coated Samples**

The electroless nickel plating process has been replaced by the Enthone process mentioned. Samples have been prepared with an alloy range of about 9% to 13% by weight phosphorous. A complete process record of the variables and the resulting plating rate and alloy composition has been prepared. See Appendix I. Samples of the 11% alloy were polished by MSFC and also sent to Continental Optics for polishing tests. The results from Continental Optics are not back to date. Samples of 11% phosphorous electroless nickel plated by OCA in California were also lapped by OCA and produced consistent results below 10 angstroms, with most readings of about 6 - 8 angstroms rms. The Enthone 11% phosphorous samples polished by MSFC appear to be of equal or better quality to the prior Stapleton deposit samples.

#### **(b) Vacuum Deposited Gold for First Optical Surface**

Samples of vacuum deposited gold produced during this contract include the replicate from the silicon carbide sample mentioned and test samples on float glass. The silicon carbide replicate sample had about a 5 angstrom surface finish as mentioned. One of the OCA nickel phosphorous plated samples was plated with vacuum deposited gold by Robert De Haye. The sample measured from 6 to 10 angstroms prior to plating the gold. The gold was deposited after rinsing the part with acetone only. The replicate returned only about 10 -12 angstroms and appeared to have contamination embedded in the gold starting surface. A second sample was prepared from one of the stainless steel (410) pieces from the ceramic coating study. This piece measure about 10 - 12 angstroms at the start. The gold did not adhere at all well to

the stainless steel and plating solution leaked in under the edges. However the center portion of the replicate was still about 10 - 12 angstroms rms.

The first XRCF test mandrel mentioned above was coated by evaporated gold also mentioned. The separation of the electroformed shell proceeded well using the new extraction fixture designed and built by MSEC. The small dimple in the part due to the machining error mentioned caused some slight problem in removing the shell and the temperature had to be reduced below that of the actual release. The removal was performed in a dry glove box and the moisture condensed was minimal although some frost occurred due to the extremely low temperature (ca -40 degrees C). The surface appears to be clean and free of condensed films.

(c) Conductive Oxides, Carbides and Refractory Metals for Improved Mandrel Surfaces

This activity is now a separate task under UAH D.O. 139 with Dr. Michele Wilson as P.I. She will continue the polishing efforts on the ceramic samples. She has prepared a series of smaller samples, located additional vendors, performed polishing tests on the Balzers coated stainless steel pieces and it appears that very beneficial results will be achieved. Also Dr. Wilson will attempt to develop similar coatings by using a combination of electron beam evaporation and ionization of nitrogen at lower temperature to coat nickel plated aluminum with titanium nitride.

(d) Develop Alternate Electrodeposit for Mandrels -

Samples of diamond turned aluminum have been coated with a hard bright nickel process using naphthalene sulfonic acid and coumarin as primary and secondary brighteners. The surface was not as level as with the electroless nickel and apparently the adhesion was not as high. Attempts to diamond machine this material showed promise in that the tool was not damaged by several tests.

The rake angle did appear to be too positive at 0 degrees and a new tool has been ordered and received which has a negative 5 degrees rake. Tests will continue to determine if this material is diamond machinable.

Samples of nickel cobalt alloy have also been prepared and a direct lapping test has been started. The sample readily produced a 20 angstrom surface free of pitting but no subsequent effort has been available to determine the best achievable surface finish.

Eighteen samples of the 10 - 12 percent phosphorous electroless nickel have been prepared from both the Stapleton and the Enthone processes.

Two of the samples from the Stapleton process were lapped with diamond (as opposed to alumina as before). These samples appear to have surface damage in the form of pitting. It is not yet clear if the pitting is material or process related. One of the Enthone parts was lapped using the same diamond process and appears to have produced a better surface. Eight additional 11% phosphorous samples from the Enthone process and ten Stapleton pieces were inadvertently machined to the extent that the nickel deposit was removed or cut through to the aluminum.

(e) Hybrid Composite / Plating Combinations

No activity has been started on this task.

(f) Non-magnetic Optical Electroforms

A copper solution suitable for thick electroforming of non-magnetic shapes has been formulated and tested for low stress deposition. No replicate optics have been produced from this process for this task to date.

## Contents of Appendices

<b>4.0 APPENDIX I</b>	<b>ENTHONE ADP (QA) ELECTROLESS NICKEL DATA</b>
Table 1	Bath Parameters and Coating Characteristics
	PARAMETERS CONSIDERED
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Reply to Attn of: EH24 (95-19)

March 21, 1995

TO: EB52/Bill Jones

FROM: EH24/Mitch Mendrek

SUBJECT: Characterization of Enthone Plating Process

The recent decision to abandon the Stapleton electroless nickel plating solution in favor of the Enthone process has necessitated characterization of the new process for deposited alloy content and plating rate. Seven, four hour plating runs were conducted using 1" x 1" x 0.063" coupons of 6061-T6 aluminum. Bath pH and reducer (hypophosphite) concentration were varied while maintaining the nickel concentration and temperature constant. The plating rate was determined by micrometer measurement of the coupons (six minimum) before and after plating. Alloy content (weight % of phosphorous and nickel) was determined by x-ray fluorescence. Hardness of the plated coupons was determined by EH22 prior to heat treatment.

Results of this work are summarized in the Table 1. In addition, Figures 1-4 show plots which should prove useful for subsequent plating runs.

Table 1. Bath Parameters and Coating Characteristics

Run No.	[Ni] (g/l)	[Hypo] (g/l)	pH*	Temp. (°F)	Composition (%P)	Plating Rate (mils/hour)	Hardness (Rc)
1	5.8	19	4.5	185	11.12	0.25	---
2	5.8	19	4.7	185	10.05	0.37	---
3	5.8	19	4.85	185	9.69	0.42	54
4	5.8	22.8	4.85	185	9.78	0.43	---
5	5.9	22.8	4.5	185	11.12	0.3	54
6	6	22.8	4.4	185	12.42	0.21	54
7	5.9	25	4.4	185	12.4	0.2	---

\* All pH measurements taken at 130°F.



In Figure 1, the alloy content (weight % P) and plating rate are plotted as a function of the pH, with reducer concentration (19 g/l), temperature (185°F) and nickel concentration (5.8 g/l) held constant. Figure 2 shows a similar plot with a reducer concentration of 22.8 g/l. In Figure 3, the alloy content and plating rate are plotted as functions of the reducer concentration for three pH levels. In Figure 4, the alloy content and plating rate are plotted as functions of pH for three reducer concentrations.

Figures 1 and 2 show that the alloy content and plating rate are strong functions of pH. As expected, alloy content decreases and plating rate increases with increasing pH. Figure 3 shows that alloy content and plating rate are virtually **independent** of reducer concentration in the range of 19-25 g/l. Figure 4 confirms this finding by showing that all alloy content vs. pH data points fall on the same curve, regardless of reducer concentration. Thus, if nickel concentration, pH and temperature are held constant, the reducer concentration may vary by 20 % without affecting alloy or plating rate. This result is significant since determination and adjustment of bath pH and nickel concentration are much less labor intensive than the hypophosphite determination. In addition, large additions of reducer make-up were shown during the CIRS project to present bath stability problems with the Stapleton process. The conclusion reached during the CIRS work was that reducer should only be added in very small, well diluted quantities while the bath is hot.

In an attempt to determine the effect of alloy content on polishability, microhardness measurements were made on six coupons representing three alloy content ranges. As shown in Table 1, the coating hardness did not vary in the range of 9.6 to 12.6 %P. The coating thickness did vary from 0.8 to 1.6 mils for the coupons tested, and the effect of thickness on microhardness is not known. Similar tests on thicker coatings are planned.

Comparison of the two processes indicates that the Enthone process is significantly more stable than the Stapleton process. To date, ten (10) plating runs have been completed with the Enthone process without a bath failure. The lower temperature (185°F vs 195°F) and reducer concentration (20 g/l vs 34 g/l) of the Enthone process are probably significant contributing factors to this stability. In addition, the Enthone process maintains a relatively high plating rate even with these lower conditions. It should be noted however, that the rates reported here are average rates for four hour runs. Longer runs will have lower average rates and witness coupons must be used if tight tolerance on the thickness is required. Finally, the Enthone process appears to yield deposits which are essentially defect free, although the data for the Enthone is limited compared to the Stapleton process. Initial studies indicate that Enthone deposits can be polished to 6-8Å surfaces.

The following points summarize this work:

- (1) The nickel deposit produced by the Enthone process is insensitive to reducer concentration over a wide range if other bath parameters are held constant.

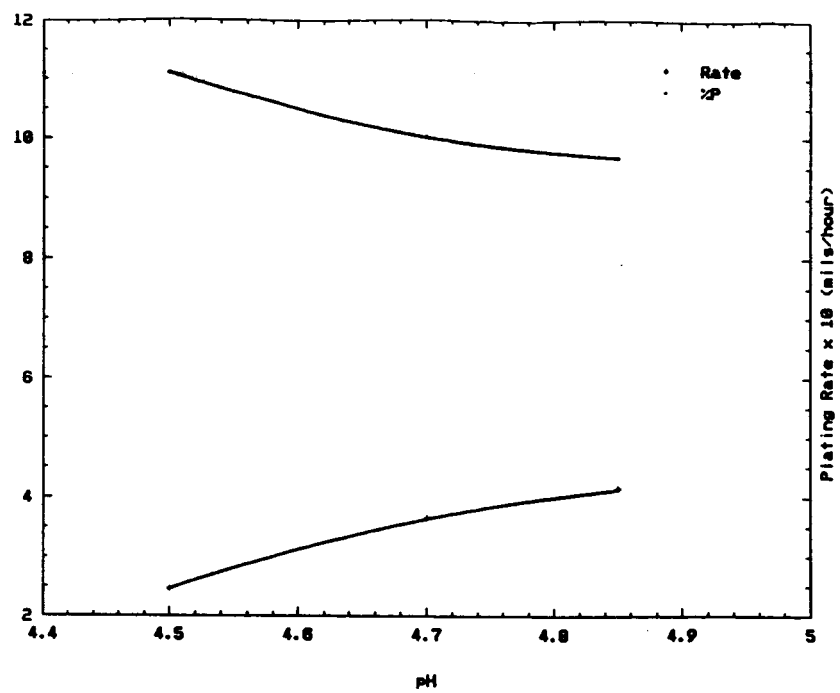


Figure 1. Alloy Content and Plating Rate vs. pH for Reducer Concentration of 19.0 g/l.

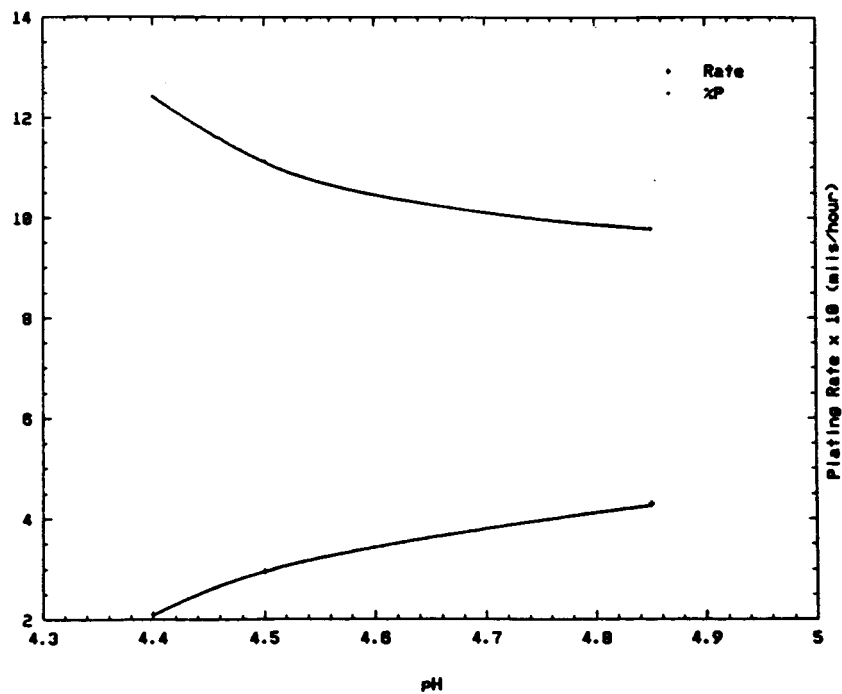


Figure 2. Alloy Content and Plating Rate vs. pH for Reducer Concentration of 22.8 g/l.

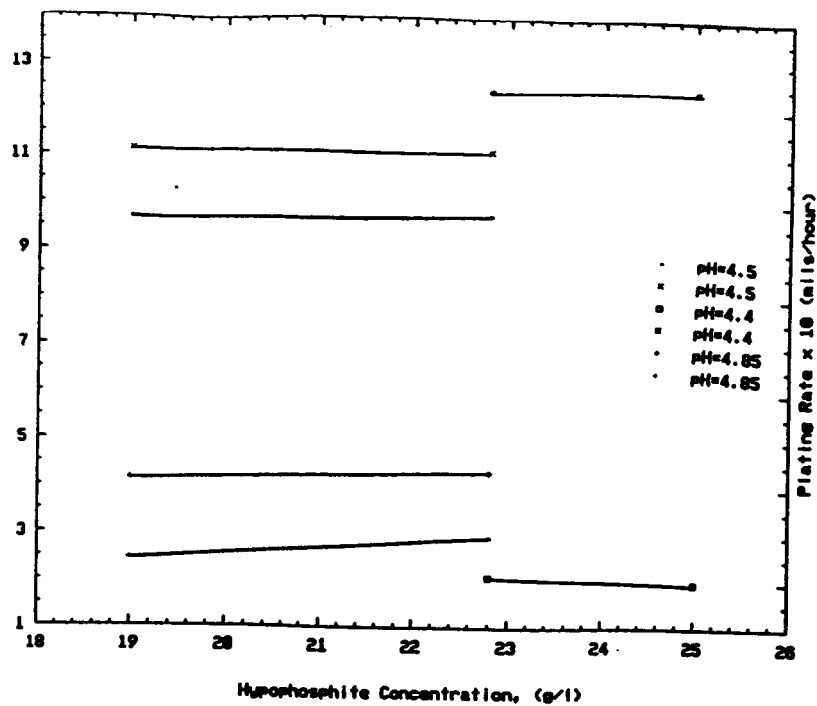


Figure 3. Alloy Content and Plating Rate vs. Reducer Concentration at Three pH Levels.

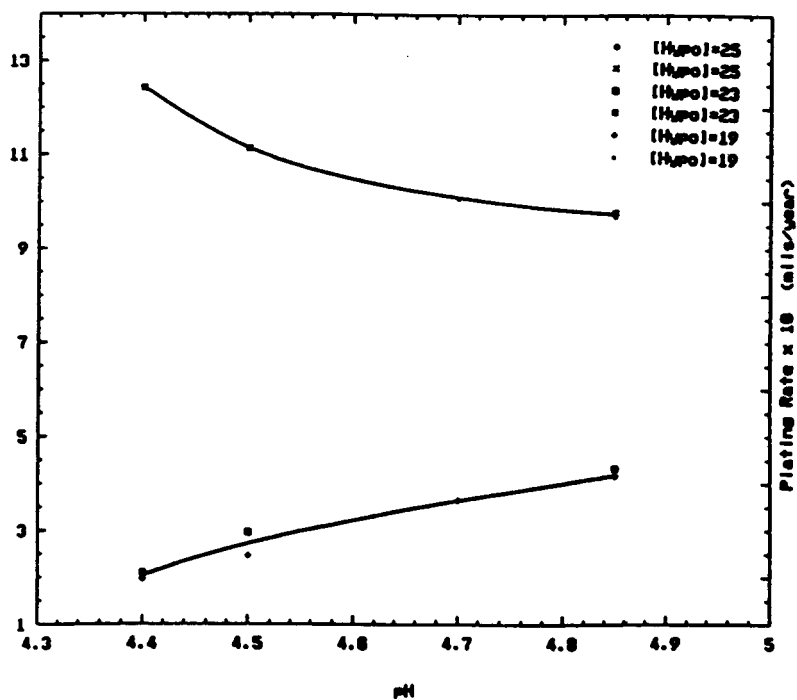


Figure 4. Alloy Content and Plating Rate vs. pH at Three Reducer Concentrations.

PERCENTILE PHOSPHOROUS VS pH OF ADP-300

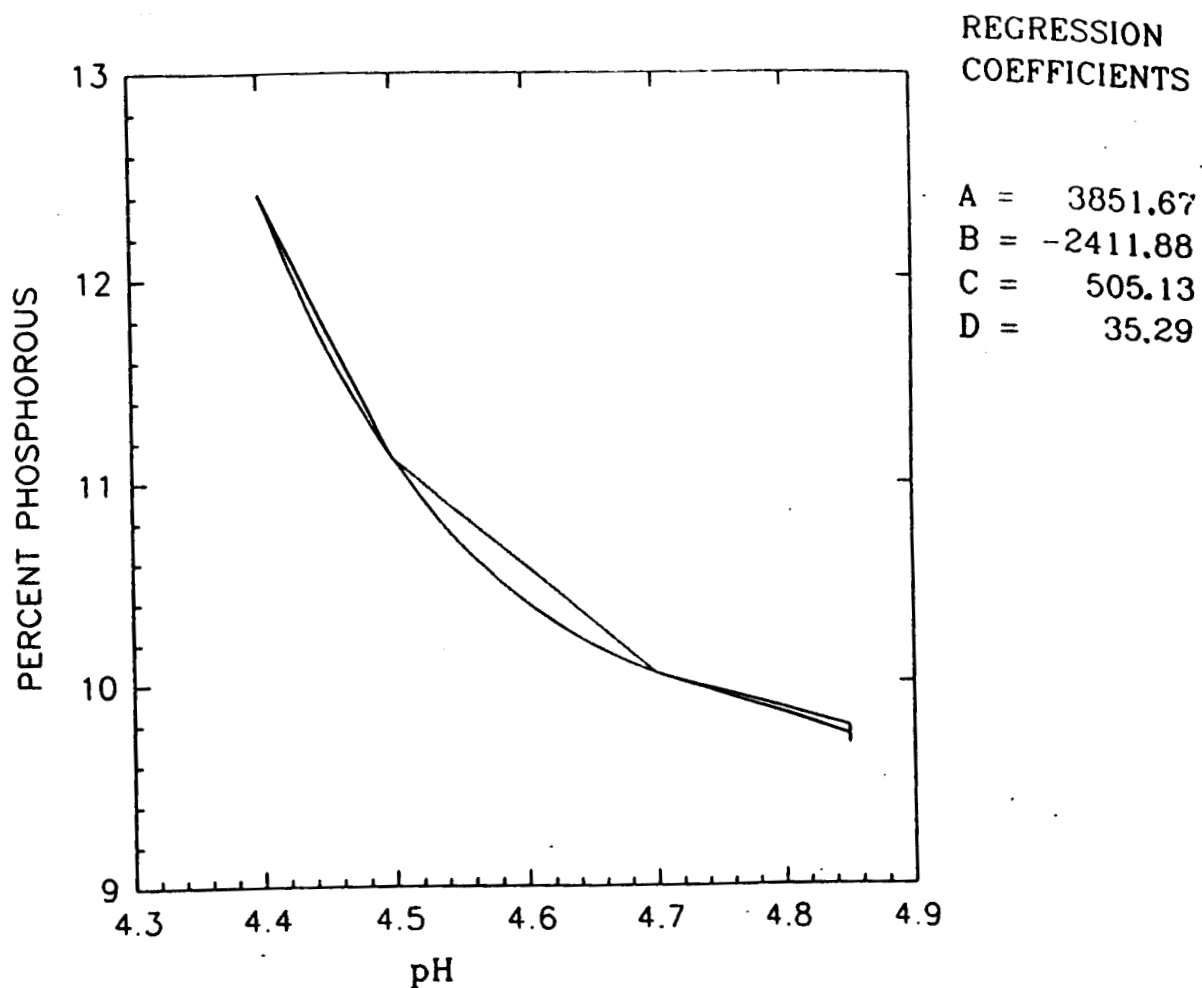


Figure 5. Alloy (%P) vs pH of Enthone ADP-300 Deposit  
Regression Fit to 3rd Order Over All Data

(2) The Enthone process is very stable.

(3) The Enthone process yields deposits which are essentially pit free and polishable.

Questions related to this work may be addressed to the undersigned at 544-2619.

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## **Appendix II      Passivation Process for Electroless Nickel**

### **Discussion:**

The use of a mandrel of very highly polished nickel phosphorous as a substrate for the replication of a high quality internal surface of deposited gold followed by pure nickel (x-ray mirror electroform) has been demonstrated. To successfully plate and remove the electroform from the polished substrate, an oxide film with low affinity for the deposited gold is required such that the electroform can be subsequently removed. The adherence of electrodeposited gold is dependent on the oxide film thickness and composition. For the case of the vacuum evaporative process gold on nickel, the spontaneously formed oxide is adequate to prevent high adhesion or atomic bonding. For nickel in air this occurs in a few minutes according to parabolic rate laws for the diffusion of nickel through the forming oxide film.

This appears to be generally true for the nickel phosphorous alloy as well although the oxide films differ in that the electroless nickel phosphorous oxide film indeed contains P - O bonds. The film thickness of the spontaneously formed oxide for the electroless nickel was measured qualitatively by AUGER and appears to be only tens of angstroms thick. By static immersion or by anodically applied current in sodium hydroxide it is possible to increase this by at least an order of magnitude. By applying a cathodic current to the nickel phosphorous part in the same media, it is possible to reduce the oxide film to near zero thickness. On two occasions with early test parts passivated in sodium hydroxide, the electrodeposited gold adhered sufficiently to prevent separation of the electroform. It was determined that the use of a cyanide gold plating solution with very high deposition potential and low efficiency was in part responsible. This is because the acid cyanide solution evolved hydrogen reducing in part the oxide film and therefore permitted metallic bonding of the deposit. Subsequently for the same passivation, the use of an alkaline non-cyanide gold process produced poor adhesion and the gold peeled in spots.

Investigation of the passivation of the electroless nickel phosphorous alloy was initially performed on Contract No. NAS8-38609, D.O. 63. During this contract it was shown that the growth of the oxide film on the alloy could be monitored in real time by potentiometric methods. It was demonstrated that the kinetic growth mechanisms of the oxide film growth took two distinctly different paths. The oxide growth changed from passivation in a sodium hydroxide solution involving four steps to a more readily controlled process with two steps when the polarization was conducted in a complexing media of sodium potassium tartrate (Rochelle salt). It was determined that if the passivating current density (or cell voltage) was raised slowly to permit con-

trolled growth of the oxide and if the process was monitored in real time then it was possible to achieve essentially the same level of adherence of the subsequent gold deposit. This is due to the repeatability of the polarization as a result of the process allowing for the observation of the extent of the film growth.

At a ramped small current density, the potential will rise slowly to a ceiling value consistent with the growth and formation of the oxide. The oxide film growth rate will then become constant at that current density. This value is maintained for a fixed time to achieve a consistent oxide film composition and thickness. It is important to first reduce any pre-existing spontaneously formed oxide on the surface prior to the passivation in order to achieve repeatable results. By measuring the surface potential with a high impedance electrode during polarization, it is possible to monitor the extent of oxide formation.

Then by discontinuing the current and continuing to monitor the potential, a decay is observed consistent with the discharge of the double layer capacitance through the film conductance. The extended or delayed decay of this potential indicates over passivation which in the case of the alkaline gold deposition causes severe lack of adherence to the extent that the gold literally peels off from the solution agitation. If the decay is very rapid by contrast then the film is sufficiently thin to still be a metallic conductor and the gold may adhere to the extent that removal is difficult or not possible.

All of the previous x-ray mirror mandrel passivation prior to the electrodeposited gold, was performed by manually adjusting the current to achieve the proper results. This required very close attention and precise response to the waveform observed. This was difficult due to the inability to predict the exact response and also due to the rather rapid response requirements on the part of the operator. Therefore a computer input - output (IO) closed loop passivation process has been developed for future hardware fabrication. This process controller consists of a PC computer, an interface IO card, and software to determine the exact response requirements and apply the appropriate change in current density (or cell voltage) to achieve the desired oxide formation.

In this process the part is first placed in a solution of sodium hydroxide, and made cathodic at 20 - 30 mA/cm<sup>2</sup> for two minutes to remove the pre-existing oxide film. The part is rinsed and transferred to the passivation process and immersed without current. The connections are made and the part is slowly made anodic by ramping the cell voltage or the applied current density to a predetermined value consistent with formation of the first plateau seen in the voltammograms (polarization plots taken with the EG&G potentiostat earlier). See figures 6 and 7.

The ramp rate is determined by the slope of the measured potential and not the current or cell voltage since this is a measure of the actual film formation. At a predetermined surface potential the cell voltage is held constant to maintain this value for about twelve seconds. The current is then abruptly discontinued by open circuit and the decay is measured. If the decay to a predetermined surface potential is within a defined window of time, the program signals that the process was successful, then the part is removed, rinsed and transferred to the gold plating solution and the mirror fabrication electroforming operation commences. If the potential decay is outside the window either too long or too short then the process is repeated from the cathodic deoxidation step.

Note that it is imperative that all process solutions be very carefully controlled to provide repeatable results. In particular if the sodium hydroxide solution is contaminated with certain metals, deposition is possible which will coat a thin layer of impurity on the precision mandrel. Also if the pH of the passivation solution is out of range then under or over passivation may occur. This will be indicated in the decay response but will require correction prior to plating of the gold. Additionally the current source must be disconnected in order to observe the decay. This may or may not occur by simply shutting off the power supply depending on the make and model.

Tests have been completed on small two inch diameter coupons and the surface has been examined by interferometry and found not to have been measurably affected by the passivation process. The computer process control was used for these tests. Further tests of the gold adherence using the computer vs the manual processing of parts is ongoing.

The software program is entitled "Passivate.pas" and is written in Turbo Pascal 6.0 by Borland. It begins with a main menu which permits selection of all the process variables and passivation parameters. The program allows for real time graphical observation of the polarization from a saturated calomel electrode placed in the solution and referenced with respect to the part (anode in this case) in addition to the applied current. The program has not been compiled and as such requires support of the Pascal source code and several drivers from the Data Translation DT 2812 IO card package. This permits updates to this new procedure. The program was written by Paul Wilkin of George Washington University with inputs for the hardware, process, interface and algorithm requirements from D. Engelhaupt of The University of AL in Huntsville and MSFC personnel. The program allows for the storage and retrieval of all pertinent data to accurately reproduce the results. Additional features allow for selection of storage and retrieval of the actual passivation data and printing of the data points if desired.

A description of the menu follows alphabetically:  
See Flow Chart Diagrams, Figures 8 and 9.

- a) Get Part Area  
Input the area of the part to calculate the current density
- c) Start Control  
After all parameters are established and connections are made the process is started
- d) Display Adjustable Parameters  
Displays the part area input, current density ramp, control resolution, passivation time, card input gain on each channel, passivation time, and decay parameters selected
- f) Save to File  
Yes or No selection  
If Yes, Name File
- g) Set Input Gains  
DT 2811 Gain on Card Dependent on Other Hardware  
Typically remains same for given configuration
- l) Set Criteria for Passivation  
The Decay time is observed for a given Threshold Potential  
If Out of Range, Warning is Given to Indicate Problem Exists  
If in Range, Indicates That Process Succeeded
- o) Set Print and Disk Options  
Yes or No, Enter Save Filename if Yes For Save
- p) Retrieve File Parameters  
Eliminates Re-entry of all Data Once Established
- r) Set Control Resolution  
Permits Large Range of Operational Conditions and Hardware
- s) Set Potential Rate  
Allows Setting of the Value of Rate of Potential Change to be Controlled by the Real Time Compensation of the Power Supply Output
- t) Set Passivation Time  
Allows the Establishment of the Time at the Predetermined Maximum Potential to Permit Controlled Growth of the Oxide
- v) Turn Graphics On/Off  
Normally Left On to Observe the Oxidation Process
- q) Quit  
Disengages Program and Hardware.



Begin  
(Control)

Start Clock

Measure Mandrel Surface Potential  
Measure Bath Current  
Calculate Potential Rate

Plot  
Potential, Current  
&  
time

Is  
Potential Rate  
>  
Target Rate?

Yes

Reduce Power

No

Is  
Potential Rate  
<  
Target Rate?

Yes

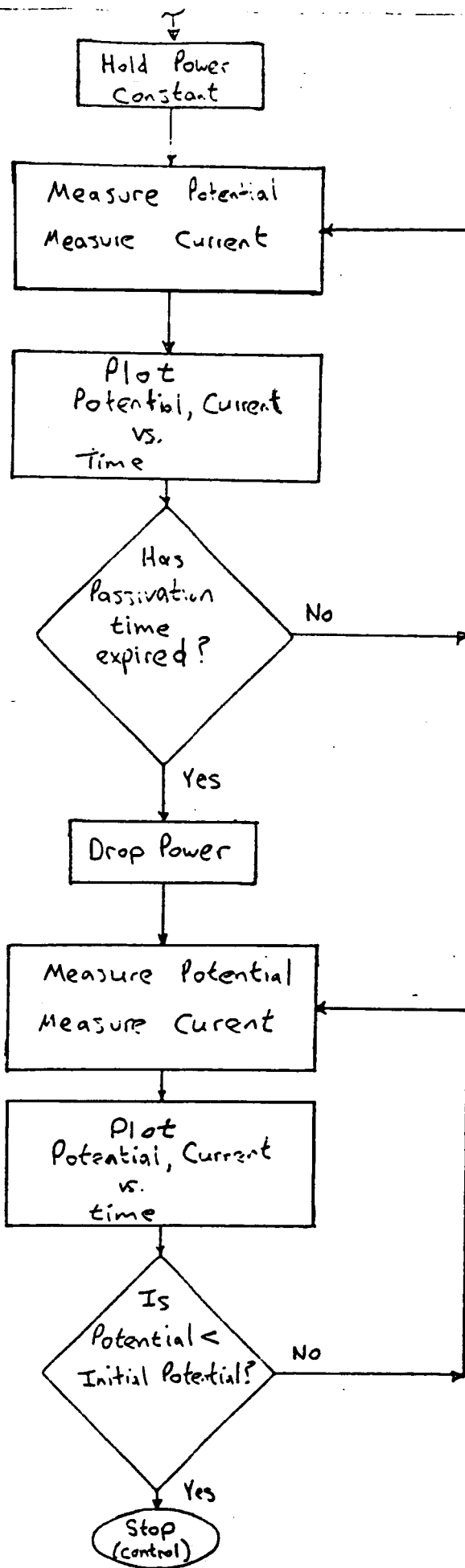
Increase Power

No

Has  
Passivation  
been reached?  
(Zero Potential)  
rate

No

Yes





a = get part area  
c = start control  
d = display adjustable parameters  
f = save parameters to file  
g = set input gains  
l = set Criteria for passivation  
o = set print and disk options  
p = get parameters from file  
r = set control resolution  
s = set potential rate target  
t = set passivation time  
v = turn graphics on/off  
q = quit



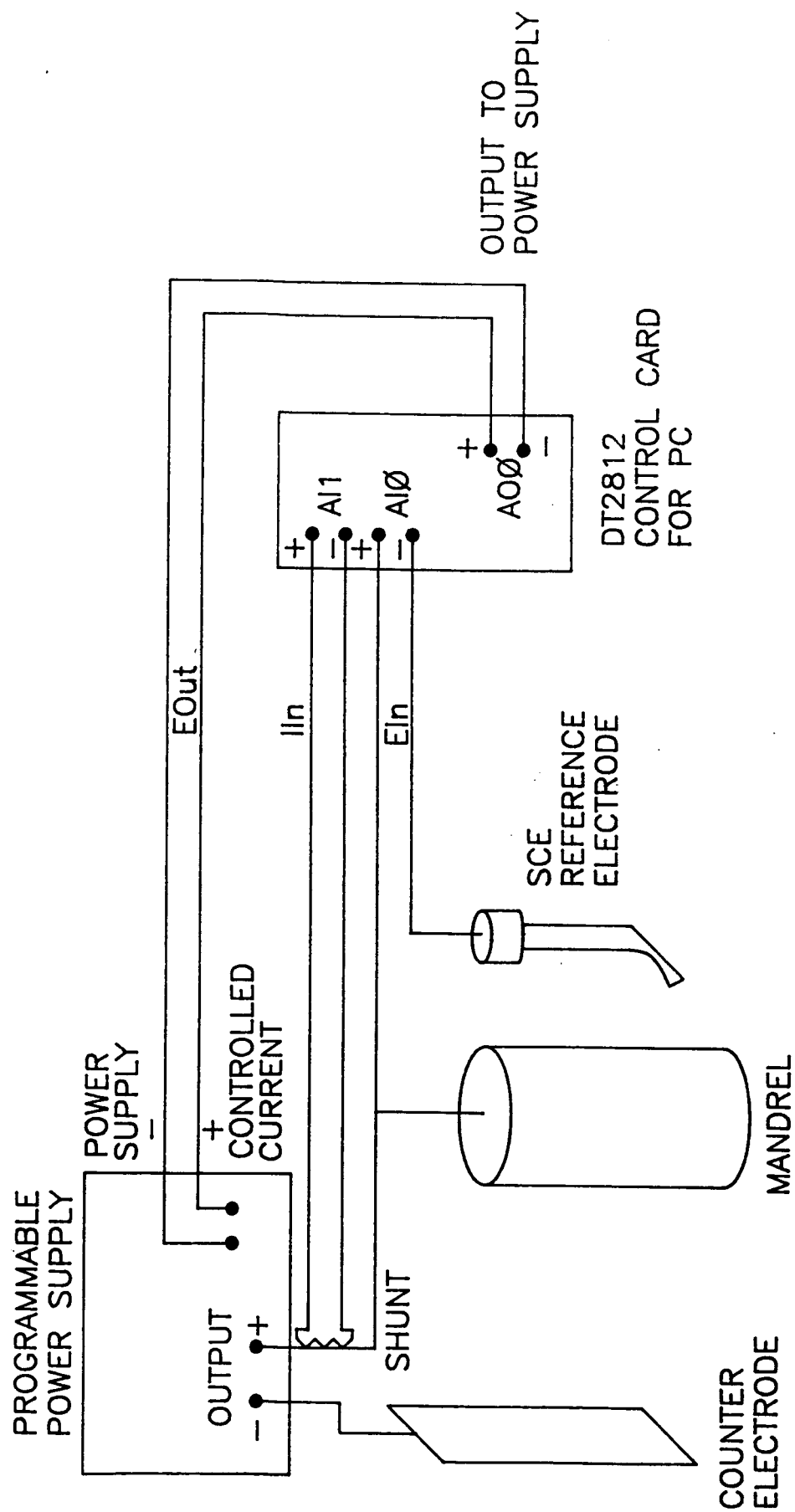


Figure 1

# AUTOMATED PASSIVATION CONTROL

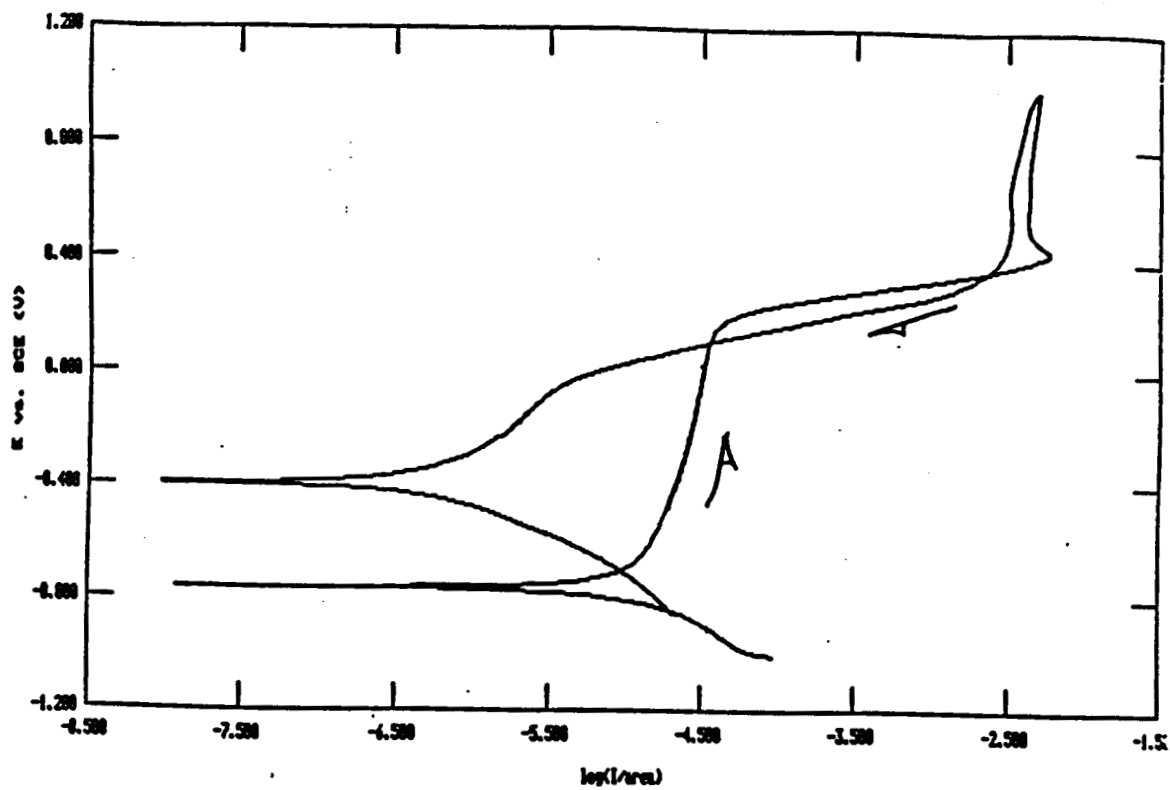


Figure (2)

0.1N NaOH  
0.1M Rochelle Salt  
0.1M  $\text{Ni}^{++}$

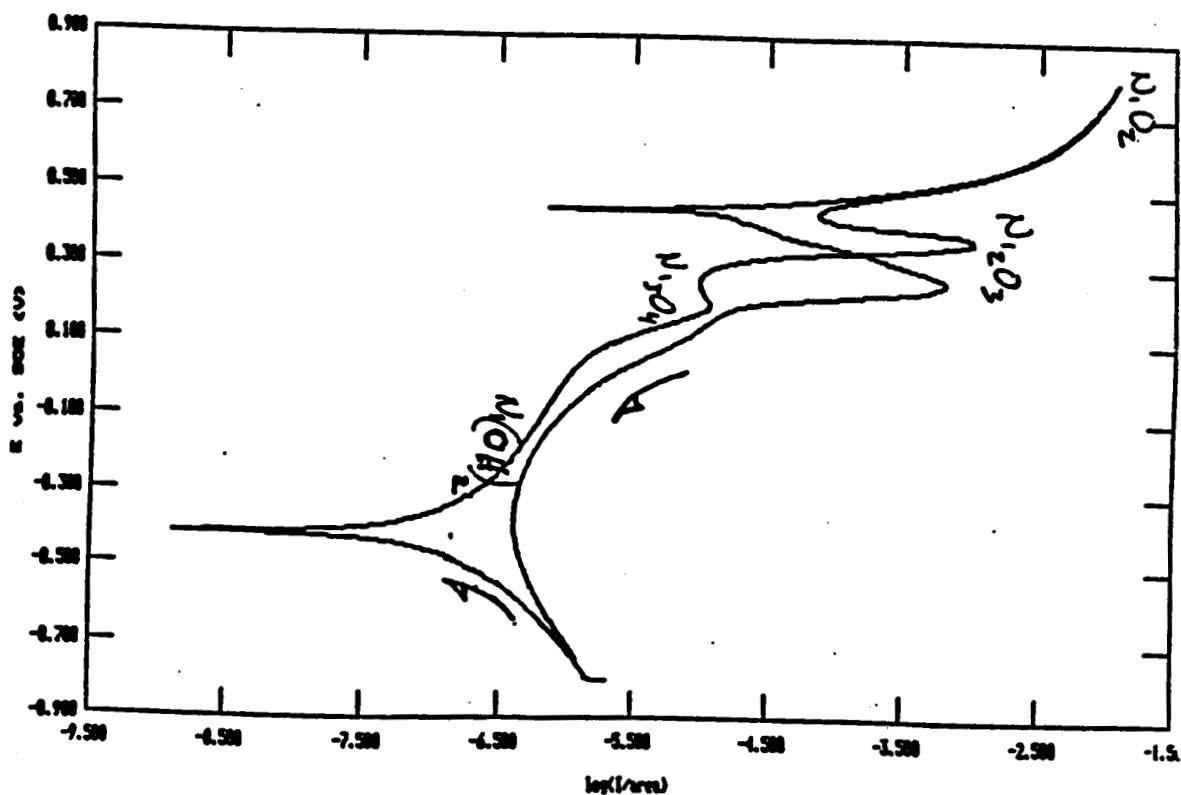
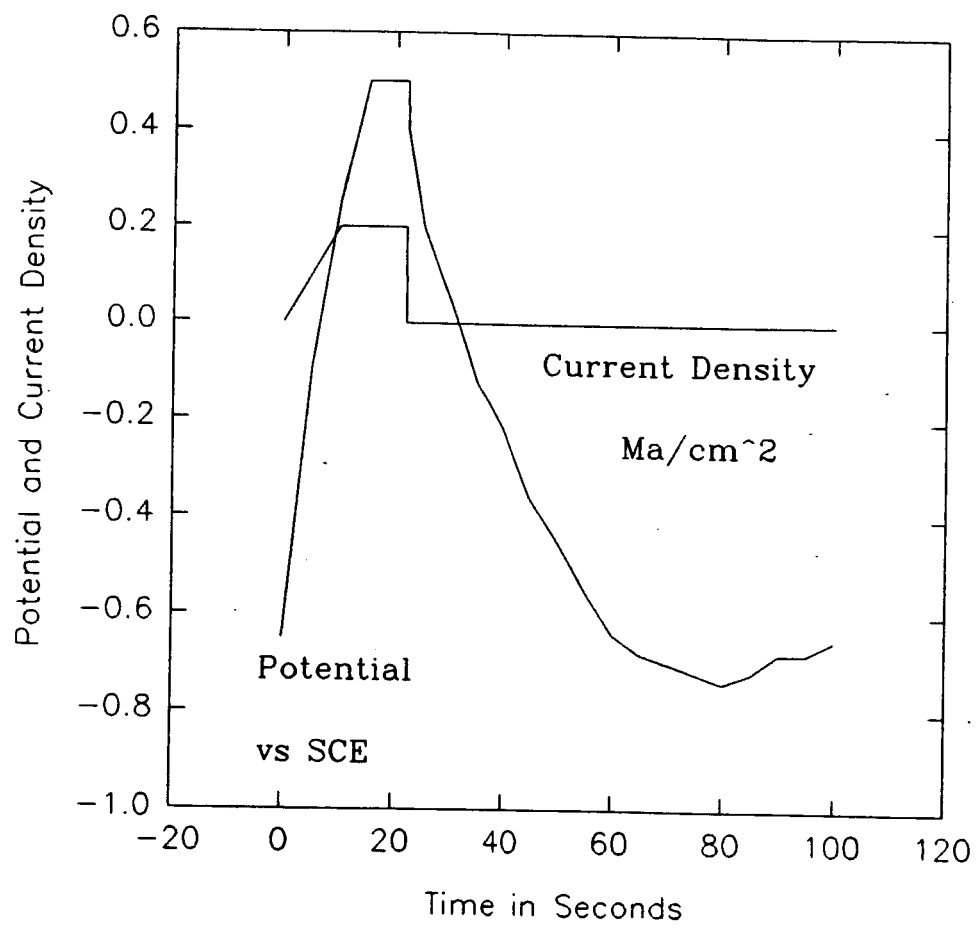


Figure (3)

0.1M NaOH R.T.

# PASSIVATION PROCESS DATA



Passivation of  
Nickel Alloy  
11% Phosphorous  
by Weight  
pH 11 Tartrate